Shear banding in crystallizing colloidal suspensions

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Abstract

We characterize the shear bands generated in simple shear flow of a crystallizing colloidal suspension. 35 volume % suspensions of poly(methyl methacrylate) colloids of diameter 0.68 µm were dispersed in the viscous solvent dioctyl phthalate and subjected to plane Couette flow. The equilibrium structure of this suspension was crystalline and flow accelerated its crystallization kinetics significantly. Confocal laser scanning microscopy and particle tracking were used to characterize the height-dependent velocity profile in the gap of the shear flow. Near each of the two boundary surfaces, a region of high shear rate flow was observed. A low shear rate region was observed at the center of the gap. The differences in the shear rate within the two banded regions were a function of the both the applied shear rate and strain. The effect of strain indicated that the shear band development was a transient phenomenon. We found that the boundary between the high shear rate and low shear rate regions correlated with the location of crystalline and amorphous regions in the gap of the shear cell, as visualized by confocal microscopy. Furthermore, the different local shear rates observed in the banded regions were consistent with the different viscosities of the amorphous and crystalline suspensions. The results demonstrate that shear banded flows accompany shear-induced colloidal crystallization, and that the bands exhibit transient behavior because the crystallization process itself is strain dependent.

Keywords: colloidal crystallization, confocal microscopy, self-assembly

1. Introduction

Above a critical volume fraction, dense colloidal suspensions undergo phase transitions in order to minimize free energy (Anderson and Lekkerkerker, 2002). Such equilibrium crystallization has been studied extensively in model colloid systems. The rate of crystallization by homogeneous mechanisms can be predicted by means of theories such as classical nucleation theory (Gasser, 2009). In contrast to equilibrium crystallization, the kinetics of crystallization under non-equilibrium conditions are not well characterized. The non-equilibrium conditions of flow have a number of effects on colloidal crystallization. First, flow can stabilize metastable structures by shifting phase boundaries (Holmqvist et al., 2005). Second, it can accelerate the kinetics of crystallization. In the second case, the rate of colloidal crystal formation depends strongly on the strength of the applied flow field relative to the randomizing effects of Brownian motion, as quantified by a dimensionless Peclet number and first identified by Ackerson and coworkers (Ackerson 1990). Indeed, application of flow has been shown by scattering to lead to a rich sequence of microstructural transitions and metastable phases (Chen et al., 1994). Here we study the relationship between flow-induced crystallization in concentrated colloidal suspensions and deviations from homogeneous shear flow, such as shear banding, in such suspensions. Quantifying the correlation between shear banding and crystallization kinetics is necessary for any predictive theory of flow-induced crystallization.

Shear banding has been observed in concentrated colloidal suspensions in a number of cases and a few studies have connected shear banding and shear-induced crystallization or melting. Holmqvist et al. studied crystallization kinetics in a charge-stabilized colloidal suspension (Holmqvist et al., 2005). At a particle concentration of 25.2 wt%, they found no effect of shear-induced phenomena such as shear banding on crystal growth rates. Cohen et al. studied steady-state shear banding in crystallized colloidal suspensions in oscillatory flow (Cohen et al., 2006). Shear banding was asymmetric about the mid-plane of the flow and it was generated by a yielding transition due to the strain amplitude of the high rate flow. Wu et al. reported steady-state shear banding in colloidal suspensions in which the location of the bands was due to the coexistence

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of amorphous and crystalline structures in a shear flow (Wu et al., 2009). The local shear rate in the crystal band was greater than the shear rate in the amorphous band and this difference was linked to the different steady-state viscosities of the two structures. Our work here complements these studies by: (i) quantifying the transient behavior of the shear bands as they develop from a suspension with initially amorphous structure; (ii) connecting the transient development of the shear bands to the flow-induced crystallization kinetics; (iii) connecting the band development to the different viscosities of the amorphous and crystalline suspensions.

Our focus in this study is shear banding which occurs at overall shear rates for which the dimensionless flow Peclet number, $Pe$, is greater than one and less than about $10^3$, $1 < Pe < 10^3$. Within this range, for suspensions with volume fraction in the coexistence or fully crystalline regions of the phase diagram, steady or oscillatory flow accelerates the production of colloidal crystals (Vermant and Solomon, 2005). Here $Pe = \frac{\gamma_x a^3}{k_b T}$ where $\gamma_x$ is the shear stress, $a$ is the particle radius and $k_b T$ is the thermal energy. In a prior study, we showed that the 35 volume% suspensions of sterically stabilized poly(methyl methacrylate) colloids underwent flow-induced crystallization in the flow generated in a spin coating device (Shereda et al., 2008). Here we study the behavior of suspensions at the same volume fraction in plane Couette flow. We find interesting connections between shear banded structure, transient crystallization behavior, and rheology.

2. Materials and Methods

2.1. Colloidal suspensions

Colloidal particle synthesis was carried out using methods described in the literature (Antl et al., 1986; Pathmamanoharan et al., 1989; Campbell and Bartlett, 2002). The resulting poly(methyl methacrylate) (PMMA) particles contained Nile Red dye, which allowed for imaging by confocal microscopy using a 488 nm laser excitation. The particles were negatively charged and interacted repulsively.

The colloids were dispersed in the viscous, non-volatile solvent dioctyl phthalate at a concentration of 35 volume percent. (This viscous solvent was chosen to shift the conditions necessary for shear-induced crystallization, $Pe > 1$, into a range accessible to confocal microscopy visualization during shear flow (Solomon and Solomon 2006; Kogan et al., 2008).) From scanning electron microscopy, the diameter of the particles was 0.68 $\mu$m and their standard deviation in diameter was 2.3%. Addition components added to the solvent were 7% photopolymer (CD501, Sartomer), 1% photoinitiator (Irgacure 2100, Ciba Specialty) and 10 $\mu$M tetrabutylammoniumchloride (TBAC). The photopolymer and initiator were added to allow immobilization of the structure developed under flow so as to characterize the crystallinity of the structure by 3D confocal laser scanning microscopy (Shereda et al., 2008). The disassociating salt TBAC was added to screen charge in the system (Royall et al., 2003) such that the 35 volume percent concentration studied here is within the fully crystalline region of the equilibrium phase diagram. In addition to the principal measurements at 35 volume%, additional measurements were conducted under dilute conditions (2.5 volume%), to assess the performance of the shear cell device, as discussed in the next section.

The steady-state rheology of the colloidal suspension prepared was measured by cone and plate rheometry (ARG2, TA Instruments) with a cone of diameter 6 cm and cone angle $2^\circ$, as reported in Fig. 1. For these measurements, the steady-state viscosity at each shear rate was measured for 600 s after an initial delay of 30 s so as to allow the system to reach steady-state. Fig. 1 shows the significant shear thinning and modest high rate shear thickening of this concentrated colloidal suspension. Measurements reported here are within the shear thinning region of the Fig. 1 flow curve.

![Fig. 1. Shear-rate dependent viscosity, $\eta$, as a function of shear rate in 35 volume% suspensions of colloidal PMMA of average diameter 0.68 $\mu$m. The solvent, as described in the text, is comprised of 7% photopolymer and 1% initiator dissolved in the viscous solvent dioctyl phthalate. A 6 cm cone geometry with an angle of $2^\circ$ was used for measurements. The preshear protocol used is described in the text. Error bars, which are standard error of the mean of three replications, are plotted, but are not much larger than the size of a datum point.](image-url)
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2.2. Plane couette shear cell

Fig. 2 shows a schematic of the shear cell constructed to allow confocal microscopy imaging of the gap region of plane Couette flow. Briefly, the flow was generated by displacement of a top plate comprised of glass of thickness 3.18 mm. The length of the plate was 9.62 cm, its width was 2.39 cm, and its maximum distance of travel was ~1 cm. The top plate was displaced with a 5-phase stepper motor (PMM3B2, Oriental电机 company ltd) mounted above the confocal microscope; (b) shows a view from top down of the shearing surfaces. Both surfaces are transparent to allow confocal imaging.

To address the possibility of wall slip, two different surfaces were tested. The first were smooth, unmodified glass surfaces. In the second, both the bottom and top plates were dip coated in a dilute solution of polydisperse PMMA particles (mean diameter ~ 2 µm) dispersed in hexane. The plates were heated to a temperature of 170°C and held for 3 hours. The melted PMMA coated the surfaces with a layer of roughness of order ~2 µm. No significant difference in measured velocity profiles was observed for either 2.5 vol% or 35 vol% suspensions of colloidal PMMA (data now shown).

2.3. Confocal laser scanning microscopy

To image the microstructure of the concentrated colloidal suspensions, we used confocal laser scanning microscopy (CLSM, Leica SP2, 100x NA = 1.4 oil immersion objective) to visualize the colloidal particles. Two kinds of experiments were conducted. The first was to determine the velocity profile by particle tracking. The second was to characterize the crystalline and amorphous microstructure developed during the flow.

In the first type of experiment, a time series of two-dimensional (2D) images at a fixed height in the shear flow were collected. Typically 25 to 400 images at 512 × 512 resolution (0.0456 µm/pixel) were acquired with a delay (exposure) time of 0.823 s. These image series were used to determine the mean suspension velocity at the gap height of the measurement, as discussed in the next section.

In the second type of experiment, a three-dimensional (3D) image volume was acquired after the specimen had been sheared and then its structure immobilized (fixed) by UV-induced polymerization. This polymerization occurred due to the monomer and initiator suspended in the solvent, as discussed in the materials section, and was initiated by illumination of a UV source (propagated through the microscope optics) onto the specimen. The structure, as discussed in Shereda et al., 2008, was rapidly polymerized in less than < 1 s with no significant distortion of the existing microstructure. These 3D images volumes were acquired across the lower half of the shear flow gap by a collecting a set of 2D images (0.0456 µm/pixel) spaced at a slice distance of 0.0814 µm. In a typical experiment about 1,000 slices were acquired parallel to the flow direction from the bottom plate to the mid-plane of the flow. These 3D image volumes were used to determine crystalline and amorphous regions in the suspensions induced by the shear flow, as discussed following.

2.4. Particle tracking method for determination of height-dependent velocity profile

The following describes the method to characterize the gap height dependence of the velocity profile in the shear cell. The method is illustrated in Fig. 3 for crystallizing suspensions comprised of a 35 volume percent solution of colloidal PMMA. In Fig. 3, the particles that appear red (dark grey) are those of the crystallizing colloidal suspension which contain Nile Red dye. Those that appear
green (light grey) are the probe particles used to characterize the velocity profile. Probe particles, used for particle tracking, are of diameter 0.71 µm. They are dispersed at a concentration of 0.5 volume%. They contain the dye Coumarin 30, which fluoresces in an emission band that is distinct from the Nile Red dye used for the primary particles. A time series of images during flow was captured at a particular height in the sample at a particular shear rate. The image plane was located at a gap height of interest for velocity measurements.

Two consecutive images, as shown in Fig. 3, and separated by a delay time of 0.823 s, were extracted from the time series for further analysis. The probe particles, which because of their dilute concentration, were widely separated, were easily located in the two samples and their coordinates in the objective plane determined by selecting two consecutive frames near the end of each time series and locating four (green) tracer particles in the nth frame and locating the same four particles in the n+1th frame. The coordinates of each of the particles were determined using the public domain software package ImageJ and the distance the particles traveled in the flow direction was divided by the delay time (0.823 s) to yield the particle velocity. The velocities of the four particles tracked were averaged to determine velocity. This was repeated for three sets of frames in each time series.

Fig. 3. Images demonstrating the particle tracking method used to measure the height dependent velocity profile in the crystallizing colloidal suspensions. See text for description of the method from which the velocity at a particular height was determined from a sequence of two images (a) and (b), acquired at the gap height of interest, and separated by a delay time of 0.832 s. Samples here shown are comprised of a 35 volume percent solution of colloidal PMMA of diameter 0.68 µm. These images are from an experiment at a height of 50 µm with a gap of 150 µm. The applied shear rate was 0.266 s⁻¹ and the strain was 40. All scale bars are 5 µm.

2.5. Quantitative image processing to determine crystalline and amorphous regions of the suspensions

The centroids of the colloids in the suspension volumes acquired by 3D confocal microscopy were located by image processing tools that have been previously described (Crocker and Grier, 1996). Centroids were determined to a resolution of ±35 nm in the objective plane and to ±45 nm along an axis perpendicular to the objective plane (Dibbble et al., 2006). The relative positions of the centroidal coordinates were analyzed to determine if a given particle was part of a locally crystalline structure. The method used is adapted from the simulations of ten Wolde et al. (ten Wolde et al., 1996), and previously used for experiments by Gasser et al. (Gasser et al., 2001), Solomon and Solomon (Solomon and Solomon, 2006) and Shereda et al. (Shereda et al., 2008). The output of this analysis was the 3D position of colloids in the suspension and the assignment of their microstructure as either amorphous or crystalline.

The local structure assessment method uses a structural measure that is sensitive to the overall degree of crystallinity but insensitive to both the type of structure (i.e. FCC vs. HCP) and its orientation in space. The method computes a vector $q_i$ for each particle that is characteristic of the local order. As computed from spherical harmonics, the $m^{th}$ component of $q_i$ is (ten Wolde et al. 1996):

$$q_{bm}(i) = \frac{\overline{q_{bm}(i)}}{\sqrt{\sum_{m=-b}^{+b} |q_{bm}(i)|^2}}$$

where

$$\overline{q_{bm}(i)} = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{bm}(r_{ij})$$

Here $i$ was the reference particle, $j$ was a neighboring particle, the coordination number $N_b$ was the number of neighboring particles, and $Y_{bm}(r_{ij})$ were spherical harmonics evaluated along the axis $r_{ij}$ connecting the $i$th and $j$th particles. For this calculation, a neighboring particle was defined as a particle located within a distance of the first minimum of $g(r)$ from the centroid of the reference particle ($i$).

To determine the local structure of a sample, each individual particle in the sample was determined to be crystalline or amorphous by calculating the bond coherence between the reference particle and each of its neighbors. Bond coherence was measured as the dot product of $q_i(i)$ and $q_j(j)$ as shown below.

$$q_{i}(i) \cdot q_{j}(j) = \sum_{m=-b}^{+b} q_{bm}(i)q_{bm}(j)$$

A bond was considered crystalline if $q_{i}(i) \cdot q_{j}(j) > 0.5$. 

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Particles with eight or more crystalline bonds were considered crystalline (ten Wolde et al., 1996).

To determine the accuracy of the algorithm two samples that were known to be amorphous and crystalline were studied. The coordination number distribution and the number of crystalline bonds distribution were compared for the two samples. It was found that the coordination number distributions for the two samples were very similar in shape and peaked at twelve (data not shown). For the number of crystalline bonds distribution, the peak in the amorphous sample was in the range of one to two while for the crystalline sample the peak occurred at twelve (data not shown).

3. Results and Discussion

3.1. Homogeneous shear flow of dilute colloidal suspensions

To establish if any deviations from simple shear flow in our shear cell device were a consequence of material properties of the crystallizing suspensions, rather than being due to possible non-idealities in the flow cell geometry itself or its alignment, we measured the height-dependent velocity profile of a dilute colloidal suspensions at shear rates that spanned the region of interest for colloidal crystallization. The results are plotted in Fig. 4 for measurements of a 2.5 vol% suspension of 0.68 μm PMMA colloids dispersed in dioctyl phthalate. Pe equals 4, 8 and 12.7 for these measurements. Thus, the experiments are in a regime in which the displacement of the colloids is dominated by the convective effects of the flow, rather than by the effects of Brownian motion. The error bars plotted are the standard error of the mean of four independent measurements. The lines, which are the predicted velocity profile in the gap of the shear flow given the velocity imposed on the top plate, agree well with the measurements. Thus, we conclude that the shear cell geometry, its alignment, and the method to characterize the height dependent velocity profile are all sufficient to conclude that the base flow is homogeneous simple shear, absent any effects of the colloids as high concentration, as addressed in the next section.

3.2. Inhomogeneous shear flow (shear banding) of a concentrated, crystallizing colloidal suspension

Fig. 5 reports results of an experiment similar to that of Fig. 4, except the volume fraction of the colloidal suspension was 35%. This volume fraction was in a regime that was both concentrated (i.e. significant shear thinning was observed) and above the crystalline phase boundary (i.e. given many days under quiescent conditions, this sample underwent the slow process of nucleation and growth to yield a polycrystalline colloidal crystal). In Fig. 5, results for Pe = 13, 17 and 23 are reported. Because Pe > 1 for these experiments, they are in a regime in which

![Fig. 4. Measured velocity profile for 2.5 volume% colloidal suspensions of PMMA particles. For these experiments, the top shearing surface, which is displaced at the velocity shown in the legend, is located at a height of 150 μm. The lines are the prediction for simple shear flow based on the known velocity of the top shearing surface.](image1)

![Fig. 5. Measured velocity profile for 35 volume% colloidal suspensions of PMMA particles. For these experiments, the top shearing surface, which is displaced at the velocity shown in the legend, is located at height of 150 μm. The lines are the results expected for simple shear flow, as measured in the case of the dilute colloidal suspensions of Fig. 4. These measurements were acquired after an applied strain, γ=10.](image2)
shear flow accelerates crystallization, according both to the predictions of Ackerson (Ackerson, 1990), as well as our own measurements, as discussed below. The lines in Fig. 5 are the expected behavior for simple shear flow based on the velocity imposed on the top plate. For the 35 volume% suspensions, deviations from simple shear flow were observed as the plate velocity (and therefore the Peclet number) was increased. These deviations were localized near the top and bottom plates of the deformation, and were roughly symmetric, in agreement with the report of Wu et al (Wu et al., 2009). The deviations increased with Pe and were highly significant at the largest Pe number.

For example, at the largest plate velocity of 40 µm/s, the velocity at a gap height ~ 20 µm was about 12 µm/s. This measurement was equivalent to a near wall shear rate ~ 0.6 s⁻¹, more than a factor of two greater than the imposed rate of 0.27 s⁻¹. Fig. 5 thus demonstrates that the 35 vol% suspension exhibited an inhomogeneous, height-dependent strain rate that is evidence of shear banding. The results are plotted in Fig. 6. As in Fig. 5, deviations from simple shear flow were roughly symmetric about the mid-plane of the flow (the mid-plane is at 75 µm). The results show that in all cases the flow could be divided into three regions – a central region of low strain rate and two regions of high strain rate adjacent to the top and bottom surfaces of the flow. Although the precision of the measurements precluded quantitative analysis, the deviations of the flow from simple shear increased with the applied strain deformation. The magnitude of the applied strain deformation for these measurements was too large to be explained by local distortion of the particle level microstructure, as observed in recent simulations (Foss and Brady, 2000) and experiments (Gao et al., 2010) for disordered suspensions. However, the question of the microstructural origin of this shear banding could be addressed by confocal microscopy direct visualization, as discussed in the next section.

3.3. Correlation between shear banding and shear-induced crystallization

At the conditions of the Fig. 6 experiments (γ = 10, 40 and 160; Pe = 23), we illuminated the suspension with UV light, induced photopolymerization of monomers dissolved in the solvent, and therefore rapidly immobilized the colloidal structure. Previous work has indicated that the time for immobilization by this method is sufficiently fast that there is no significant change in the particle-level microstructure before and after photopolymerization (Shereda et al., 2008). After immobilization, the specimens were imaged in 3D (up to the half-gap of the flow) by confocal microscopy. Image processing yielded the coordinates of all the particles as well as an identification of each particle as either crystalline or amorphous, based on the bond order parameters of ten Wolde et al (ten Wolde et al., 1996). Rendering of the colloidal microstructure are reported in Fig. 7. Fig. 7 shows that this suspension underwent shear-induced crystallization and that the progress of the crystallization was dependent on the magnitude of the applied strain.

Comparing Figs. 6 and 7 addresses the microstructural origin of the shear-banded flow discussed in the previous section. First, the results show that the 35 vol% colloidal suspension underwent shear-induced crystallization (Fig. 7) in the same strain deformation range for which shear banded flow was observed (Fig. 6). Second, just as a near wall region of high strain rate was observed in the measurements of shear banding, so was a crystalline region observed in that same near wall region. Thus, we infer correlation between the shear banded flow observed by par-

![Fig. 6. Strain dependence of the velocity profile measured in the gap between the shearing surfaces. The data show that the deviations from simple shear increase with the applied strain. For all experiments gap = 150 µm, shear rate = 0.266 s⁻¹ and Pe = 23.3. The line represents the results for simple shear flow, as measured in the case of the dilute colloidal suspensions of Fig. 4.](image-url)
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particle tracking and the progress of shear-induced crystallization in the suspension observed by analysis of 3D image volumes acquired by confocal microscopy.

Based on the comparison of Figs. 5 and 6 with Fig. 7 we hypothesize that: (i) the viscosity of the crystalline suspension is less than the viscosity of the amorphous, disordered suspensions, because the shear rate in the crystalline region of the flow is greater than the shear rate in the amorphous region; (ii) that on start-up of steady-shear, the viscosity evolves from a high value characteristic of the disordered suspension to a low value characteristic of the crystalline suspension, because the strain requirements for crystallization at this gap dimension require approximately 160 units of strain. These hypotheses were addressed by cone and plate rheology, as discussed in the next section.

3.4. Effect of crystallization on suspension rheology

Fig. 8 reports the results of cone and plate rheology of the 35 volume% colloidal suspension. Samples were pre-sheared at a high rate prior to the tests to insure an initial state of a metastable, disordered microstructure. The experiments were conducted at an applied shear rate that brackets the region of interest of the direct visualization experiments reported in Figs. 6 and 7. The rheological responses, which are each the average of three replications, were strain (or time) dependent. This transient response persisted over a much longer strain than could be explained by structural distortion of the amorphous microstructure. Such microstructural changes, because they involve structural distortion (anisotropy) on the order of a particle diameter, are anticipated to result in transient responses of ~ one strain unit or less. Instead, the transient rheology here observed required approximately 100 strain units or more to generate a steady-state response. This strain requirement was very similar to that found for shear banding (observed in Fig. 6) and for shear-induced crystallization (observed in Fig. 7). Moreover, the decrease in viscosity from the initial state to the steady-state was consistent with the Fig. 6 and 7 measurements. In particular, Fig. 6 showed that the shear-banded region close to the shearing surfaces was at a higher shear rate then the region in the center of the flow. Furthermore, the direct visualization of Fig. 7 showed that the near wall region was crystalline, and that the steady-state microstructure of the suspension was also crystalline. Thus, the different shear rates of the shear banded regions are consistent with the rheology of the different microstructures observed for them.

4. Conclusions

This study has shown that the transient process of shear-induced crystallization in plane Couette flow is accom-
panied by shear banded flow. The equilibrium structure of the 35 vol% suspension studied were in the fully crystalline region of the phase diagram. Direct visualization with confocal microscopy showed that the system progressed from an initially amorphous, metastable microstructure to a fully crystalline microstructure. At the gap height studied, 150 µm, this crystallization process required about 160 strain units at Pe = 23. At these same conditions, particle-tracking measurements of the height-dependent velocity profile showed that the flow deviated significantly from simple shear. The local shear rate in the near wall regions of the flow was as large as a factor of two greater than the flow in the center of the gap. These differences in the velocity profile were consistent with the transient rheology of the crystallizing suspensions, which showed about a factor of two decrease in the viscosity over a strain interval of approximately 100 units. The results demonstrate the complex coupling between flow and crystallization in concentrated colloidal suspensions. In addition to the effect of flow accelerating the kinetics of crystallization, the crystallization process itself feedbacks on the local deformation, thereby generating shear banded flow that is sensitively linked to the progress of the crystallization.

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